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# Quantitative X-Ray Powder Diffraction Analysis of Air Particulate Samples

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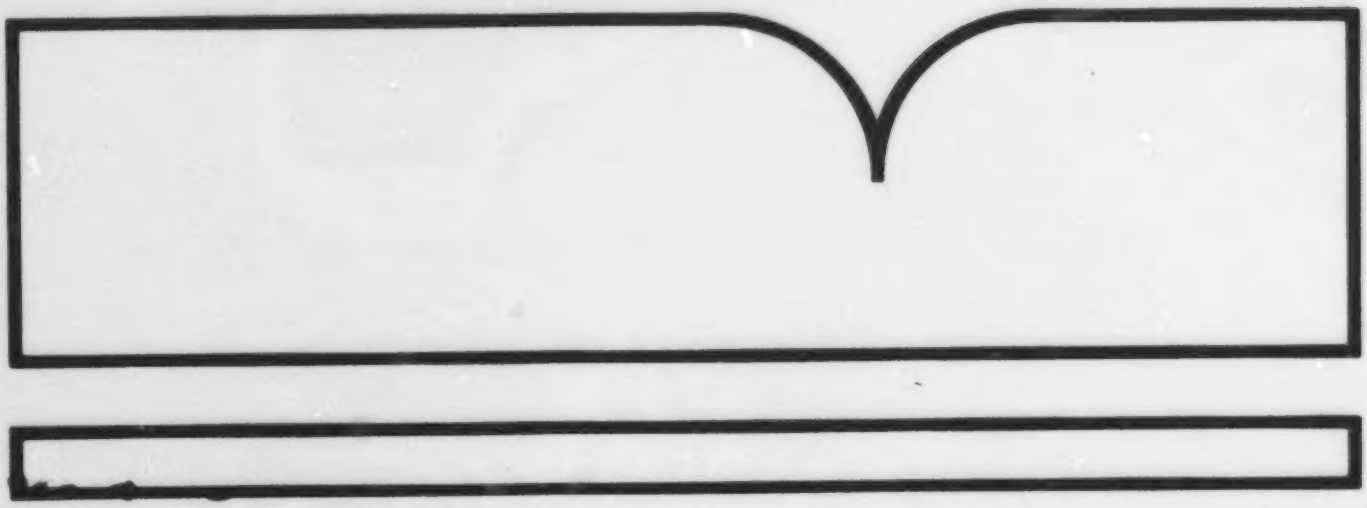

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This system was used to analyze 18 pairs of samples of the Houston aerosol. The results of this analysis when combined with the measurement of the elemental concentrations by XRF analysis give additional discrimination in source receptor models.

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# QUANTITATIVE X-RAY POWDER DIFFRACTION ANALYSIS OF AIR PARTICULATE SAMPLES

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# QUANTITATIVE X-RAY POWDER DIFFRACTION ANALYSIS OF AIR PARTICULATE SAMPLES

## Introduction

X-ray powder diffraction analysis (XPD) has long been recognized as a powerful method for the chemical characterization of crystalline compounds[1]. This technique is a promising method for the characterization of atmospheric aerosol particles and there are several reports of such applications[2-5]. However the method has not been widely applied principally because the procedures involved in conventional XPD are poorly adapted to the analysis of aerosol deposits on filter substrates. Furthermore, because of the minute quantities of materials available for analysis, measurement times were excessively long and the results were more qualititative than quantitative.

We have recently developed an automated XPD instrument with which it is possible to non-destructively analyze atmospheric aerosol samples for the concentrations of the major crystalline compounds. The system is unique in its use of a position-sensitive wire chamber counter and an on-line data processing system for rapid compound identification and quantification[6].

The instrument is optimized for the analysis of particulate aerosol samples collected with dichotomous air samplers. These air samplers separate the particles into two distinct particle size ranges, 2-15 μm diameter (coarse) and 0-2 μm (fine) particles, before deposition onto two filter substrates. Total mass loadings of up to 300 $\mu g/cm^2$ on the fine fraction filter are possible with a cellulose ester filter substrate before it becomes clogged. The coarse fraction can have somewhat more mass deposited on it. Teflon* substrate material can have mass loadings of up to 200 $\mu g/cm^2$.

The Houston aerosol was monitored at several locations during the second week of September, 1981 and the samples were analyzed by a variety of techniques. As part of the analysis of this aerosol, we have measured the crystalline material on 18 pairs of samples taken during this time on teflon substrates with a dichotomous sampler. Although these samples were acquired primarily for elemental analysis and as a consequence were too lightly loaded ($\approx$30 $\mu g/cm^2$ total mass loading) for optimum XPD analysis, the results do illustrate the usefulness of this approach in source receptor modeling of the urban aerosol.

## Description of Instrument

Figure 1 shows a schematic of the XPD instrument. It consists of a conventional 800-watt copper anode x-ray diffraction tube mounted on a $\theta$-$2\theta$ goniometer in a Bragg-Bretano diffractometer geometry. The samples are processed as they are received from the dichotomous sampler with no remounting . Computer controlled slits are used to collimate the x-ray beam onto the sample and to limit the field of view of the x-ray detector to that part of the sample which is irradiated by the x-ray beam.

The usual single slit detector is replaced with a position-sensitive proportional wire chamber which enables the parallel acquisition of data over an extended angular range[7]. The sealed xenon-filled detector is sensitive over an angular range of up to 7° in $2\theta$ with a position resolution of 0.24°(FWHM), comparable to that achieved in normal slit diffractometers.

The obvious advantage gained from such a detector is the increased data acquisition rate due to the equivalent multiple detecting element. We observe a 50-fold increase in counting rates compared to a single slit system. A secondary advantage is that the use of the extended detector causes data from the same diffraction angles to be acquired over a range of sample orientations. This results in an averaging process in which many microcrystals are oriented in the proper direction for diffractions resulting in increased sensitivity and some averaging over possible preferred orientations. This can be especially significant for the case of lightly loaded coarse particle filters where the total number of particles contributing to the diffraction signal might be statistically small.

The positions of the detected x-rays are converted to digital form using a time-to-amplitude convertor, transformed into equivalent 2θ values and then stored in the computer memory of a Texas Instruments 9900* microprocessor. This microprocessor also controls the goniometer and slits and inserts samples from a sample tray. The entire system is under the control of a Digital Equipment Corporation LSI II* computer which is also used to perform data analysis on previously acquired spectra while the microprocessor accumulates data from the current sample. This feature increases analytical output since a typical data acquisition interval for an aerosol sample is approximately two to twelve hours.

Data Analysis

The use of an on-line computer greatly facilitates the data analysis by providing rapid and convenient interpretation of the diffraction spectrum which is then followed by immediate conversion into compound concentrations in the aerosol. Since most filter substrates employed in typical air sampling programs contain both interfering lines and continuous scattered intensities[8,9], we subtract from the unknown spectrum a normalized background profile obtained from a blank filter. This both improves the signal to noise and reduces the curvature of the background. If the filter substrate is teflon, the sample spectrum is first shifted (usually less than 0.1 channel) to make the peak centroids of the strong teflon peaks the same as the centroids in the background spectrum. The remaining spectrum is then analyzed for diffraction peaks using a peak fitting subroutine. The computer software has been designed to utilize a color graphics terminal to overlay the peak analysis with the raw spectrum to verify the peak analysis. The resulting list of peak positions and intensities is used as the input data set to a chemical compound search-match routine.

The search-match procedure used in the present system incorporates certain assumptions regarding aerosol composition which greatly simplifies the algorithm. In particular, the library of possible compounds is currently limited to approximately 77 of those most likely encountered in typical aerosols. Many of these compounds are minerals which are commonly measured in aerosol samples. The search-match procedure proceeds by comparing the most prominent lines in the unknown spectrum to the most prominent lines in the stored spectra associated with the standard compounds. A figure of

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California, the U.S. Environmental Protection Agency or the U.S. Department of Energy to the exclusion of others that may be suitable.

merit which incorporates both the quality of the match-up in angle and in the intensities of the respective lines is calculated for each identified compound. The lines corresponding to the compound with the highest figure of merit are subtracted proportionately from the data set and the process is then iterated until no more candidate compounds are matched. Residual diffraction peaks not attributed to the library of compounds are listed in order that additional search-match procedures can be performed if necessary.

Because of the large number of lines associated with a given compound, the relatively poor peak-to-background ratio exhibited by the lightly loaded filters and the possibility of peak overlap from the various compounds on the filter, some ambiguity in compound identification can occur for the less abundant compounds. For this reason, the list of possible compounds must be examined carefully and some judgment must be exercised by the analyst in assessing the likelihood of certain compound identifications. These judgments are based on the number of prominent lines which are identified out of the total possible and the compatibility of the assignment with measured elemental abundances as measured by x-ray fluorescence. The graphics terminal and a digital plotter are used to facilitate this evaluation. The final analysis gives an estimate of the concentrations of compounds found and their associated error. An estimate of the elemental concentrations is also produced for convenient comparison with XRF analysis. A list of the instrumental detectability for compounds which were not observed can also be produced.

Calibration of Instrument

The absolute concentrations of the compounds extracted from the peak list are assigned on the basis of experimentally measured calibration coefficients which relate the counting rate in selected peaks in a spectrum of a prepared standard to the mass concentration of that compound. These standards were prepared from either laboratory reagents or mineral samples. The particles were ground to a fine powder with a ball mill and then suspended in an air flow and collected on a filter substrate using a conventional dichotomous sampler equipped with an inlet which limited the particle size to less than 20 μm. The masses of the prepared standards were determined either by beta gauge or by x-ray fluorescence analysis assuming a stoichiometric ratio to some easily measured element. The fine fraction sample was then analyzed in the same way as the aerosol samples. Asssignment of concentrations to compounds in the unknown spectrum then assumes that the same linear relationship exists between the total diffracted intensity associated with one or more prominent lines in the diffraction and the amount of material present.

Sources of Error

A quantitative analysis of the most probable errors associated with XPD analysis of aerosol samples is a complicated problem. The subtraction of substrate background and the extraction of peak locations and intensities are relatively straightforward procedures and their precision can be estimated assuming Poisson counting statistics and applying well-developed mathematical models. In calculating both the intensity error and the detectability for individual compounds, the background in the original spectrum is used. Similarly, the accuracy of prepared standards and the related calibration factor can be estimated from fundamental principles.

However, significant systematic errors in the analysis can result from the variability of the diffraction patterns obtained from different samples of the same chemical compound or mineral. Although the locations of diffraction peaks are fixed, the relative intensities of peaks within a diffractogram for a particular compound can vary in response to several unpredictable factors which can be associated with differences in source form or sampling methods. The most serious problems occur when the distribution of particle orientations is not completely random, due either to preferential orientation of particles with respect to some axis on the sample, or when the number of particles present in the lightly loaded sample does not represent a statistically random distribution. The potential lack of consistency in relative peak intensities can be compensated by basing the diffraction intensity for a given compound as a sum over several diffraction lines. However, in cases where the quantitative determination of minor constituents depends critically on the subtraction of more intense and possibly interfering patterns, the analytical error associated with this measurement must reflect this uncertainty.

The preferential orientation problem is illustrated in Figure 2. Figure 2a shows the spectrum obtained for a standard sample of mascagnite $(NH_4)_2SO_4$. Figure 2b shows the spectrum obtained from sample number 224302F in the Houston data set. It exhibits a spectrum dominated by components similar to 2a. Figure 2c shows the spectrum for sample 224307F which demonstrates a predominance of lines overlapping the lines of 2a but with totally different relative intensities. The simplest explanation for this effect in terms of XPD invokes a mechanism whereby the mascagnite crystals are in some manner aligned preferentially in a given direction on the filter. This could be explained by transformations which occur after the particles have been collected. One observes that the cases of preferential alignment did tend to predominate in the overnight samples where relative humidity effects could be significant. The search-match algorithum uses two calibration coefficients for regular and aligned components of mascagnite and adds them in the final analysis. Although it is still possible to obtain quantitative estimates for the amount of mascagnite even in the case of preferential alignment, the error is correspondingly increased due to this alignment artifact.

An additional problem can occur for systems in which the individual crystalline domains are too small a size to generate a significant coherent x-ray reflection. In these cases the diffraction peaks can be broadened even to the point where a given compound is not observed.

An additional variance of about 30% arises for some minerals which have different calibration coefficients for samples from different widely separated sites. Some reduction in the error associated with this variance can be achieved for the case of aerosol analysis by obtaining standards representing local sources of the material of interest. This will be especially useful in source receptor modeling where samples can often be collected of sources which will be important in receptor models. However, since this is not always possible, this variance represents a limitation of this technique.

The results of XPD analysis of the 18 coarse fraction Houston samples are presented in Table I. These samples were collected sequentially with a sampling time of 12 hours. The average calcite concentration in these samples is 7.3 $\mu g/m^3$ with very little diurnal variation while the total mass loading varies considerably. The average quartz concentration,

however, is about 15% of the total mass loading and varies with it. Although large concentrations of mascagnite were measured on the samples, when the concentrations were corrected for the 10% mixture of fine particles on the sample, the average coarse concentration of mascagnite is only 0.3 $\mu g/m^3$. Figure 3a shows a plot of the concentration of silicon calculated from the concentration of quartz from XPD as a function of the elemental concentration of silicon determined by XRF. Figure 3b is a similar plot for the calcium concentration from XPD calcite as a function of elemental calcium from XRF. This figure shows that in the Houston coarse aerosol, both calcium and silicon are highly correlated with specific mineral species.

The results of XPD analysis of the 18 fine fraction Houston samples are presented in Table II. These samples contained predominantly mascagnite (49%) which unfortunately has a large number of lines which makes identification of other components difficult. The samples were also lightly loaded (≈ 100 $\mu g/cm^2$ total mass) which also makes further compound identification difficult. There is a large diurnal variation in the mascagnite concentration as well as a large variation in the fraction that exhibits preferred orientation. The reasons for this large diurnal variation are still being studied. The double salt $PbSO_4$-$NH_4SO_4$ was the other compound found on many samples. This salt accounts for about 70% of the elemental lead concentration. Whether this salt is produced in the aerosol or is the result of conversion on the filter has not yet been determined.

These samples provide interesting information on the Houston aerosol which will need further analysis to determine their significance. The combination of this data with results from other analytical methods performed during the same sampling period of the Houston study should improve the source receptor modeling of this aerosol.

## Summary

Although the samples used in the present study had mass loadings less than the 200 $\mu g/cm^2$ required for optimal XPD analysis, we were none the less able to observe measureable concentrations of several compounds of interest in source receptor modeling. Detectabilities of better than 5 $\mu g/cm^2$ can be achieved for many environmentally interesting compounds using this instrument. We have demonstrated that it is possible to achieve convenient, quantitative and non-destructive analysis of particular aerosol samples which require detailed analysis for evaluation of specific pollution sources and their health effects. Although x-ray powder diffraction is not as precise as x-ray fluorescence and is more difficult to perform, the information it provides on the chemical composition of aerosol samples may lead to more accurate apportionment of particulate material in aerosol samples to specific sources and lead to improved pollution control strategies.

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W. Searles and R. Gatti assisted in the development and calibration of this instrument.

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TABLE I XPD ANALYSES FOR COARSE FRACTION ($\mu g/m^3$) HOUSTON SAMPLES

| Date/Time | Calcite | Quartz | Mascagnite[a] Meas. | Mascagnite[b] Net | Dolomite | Other[d] | Total[c] Mass |
|---|---|---|---|---|---|---|---|
| 9/10/0700 | 5.7 | 6.3 | 2.2 | 0.0 | 2.9 | -- | 38.4 |
| 9/10/1900 | 4.8 | 4.5 | 2.6 | 0.0 | -- | 0.3 Ps | 22.6 |
| 9/11/0700 | 4.9 | 4.7 | 3.6 | 0.2 | -- | -- | 23.2 |
| 9/11/1900 | 3.1 | 2.2 | 3.0 | 1.4 | -- | -- | 13.7 |
| 9/12/0700 | 4.0 | 3.4 | 4.3 | 0.0 | -- | -- | 17.6 |
| 9/12/1900 | 4.7 | 3.0 | 2.4 | 1.0 | 1.7 | -- | 18.2 |
| 9/13/0700 | 9.0 | 5.0 | 3.6 | 0.0 | 1.3 | 0.6 Mg,0.5 Ru | 34.3 |
| 9/13/1900 | 5.8 | 1.8 | 1.7 | 1.1 | -- | -- | 9.6 |
| 9/14/0700 | 4.9 | 2.0 | 2.1 | 0.5 | -- | 0.3 Mg | 21.2 |
| 9/14/1900 | 9.2 | 1.6 | 0.2 | 0.0 | 0.5 | 0.3 He,0.9 Ha | 14.5 |
| 9/15/0700 | 9.4 | 5.4 | 1.2 | 0.0 | -- | 0.5 Ps | 29.6 |
| 9/15/1900 | 10.1 | 5.8 | 1.6 | 0.7 | -- | -- | 29.8 |
| 9/16/0700 | 9.4 | 4.6 | 1.6 | 0.0 | -- | -- | 34.8 |
| 9/16/1900 | 6.6 | 1.2 | 0.2 | 0.0 | 2.2 | 0.5 Ha | 11.9 |
| 9/17/0700 | 11.4 | 4.2 | 0.8 | 0.2 | 1.0 | 1.0 Th,0.5 Ps | 30.3 |
| 9/17/1900 | 12.9 | 4.3 | -- | -- | -- | 1.5 Ha | 24.7 |
| 9/18/0700 | 11.5 | 4.5 | 1.3 | 1.3 | -- | 1.2 Ha | 26.8 |
| 9/18/1900 | 13.5 | 4.5 | 0.3 | 0.3 | -- | 0.6 Ha | 45.3 |
| AVERAGE | 7.3 | 3.8 | 1.9 | 0.3 | | | 24.8 |

[a]Measured concentration on filter

[b]Net concentration after subtraction of 10% fine fraction on filter.

[c]Not measured by XPD; provided by EPA.

[d]Ha = Halite; He = Hematite; Mg = Magnetite; Ps = Ammonium Lead Sulfate Ru = Rutile; Th = Thenardite.

TABLE II - XPD ANALYSES FOR FINE ($\mu g/m^3$) FRACTION HOUSTON SAMPLES

| Date/Time | Mascagnite | % Preferred | Lead Ammonium Sulfate | Total[a] Mass |
|---|---|---|---|---|
| 9/10/0700 | 23.0 ± 7.0 | 0 | 1.1 ± .4 | 56.3 |
| 9/10/1900 | 12.0 ± 4.0 | 8 | 1.6 ± .5 | 60.8 |
| 9/11/0700 | 34.0 ± 10.0 | 3 | — | 55.3 |
| 9/11/1900 | 16.0 ± 5.0 | 54 | -- | 52.9 |
| 9/12/0700 | 46.0 ± 16.0 | 9 | — | 46.3 |
| 9/12/1900 | 14.0 ± 5.0 | 34 | 0.8 ± .3 | 45.1 |
| 9/13/0700 | 39.0 ± 11.0 | 2 | 0.9 ± .3 | 73.4 |
| 9/13/1900 | 6.0 ± 2.0 | 54 | 0.8 ± .3 | 28.3 |
| 9/14/0700 | 16.0 ± 5.0 | 6 | 1.0 ± .3 | 47.5 |
| 9/14/1900 | 3.0 ± 1.0 | 18 | -- | 17.4 |
| 9/15/0700 | 12.0 ± 4.0 | 0 | 0.5 ± .2 | 28.9 |
| 9/15/1900 | 9.0 ± 3.0 | 24 | 1.3 ± .4 | 53.5 |
| 9/16/0700 | 16.0 ± 5.0 | 3 | 1.1 ± .4 | 47.5 |
| 9/16/1900 | 2.0 ± 0.7 | 40 | 0.4 ± .2 | 10.8 |
| 9/17/0700 | 6.0 ± 2.0 | 9 | 0.8 ± .3 | 27.1 |
| 9/17/1900 | 1.5 ± 0.5 | 29 | 1.3 ± .4 | 18.0 |
| 9/18/0700 | 0.5 ± 0.3 | 100 | 0.5 ± .2 | 13.8 |
| 9/18/1900 | 0.3 ± 0.2 | 100 | — | 12.6 |

[a]Not measured by XPD; provided by EPA.

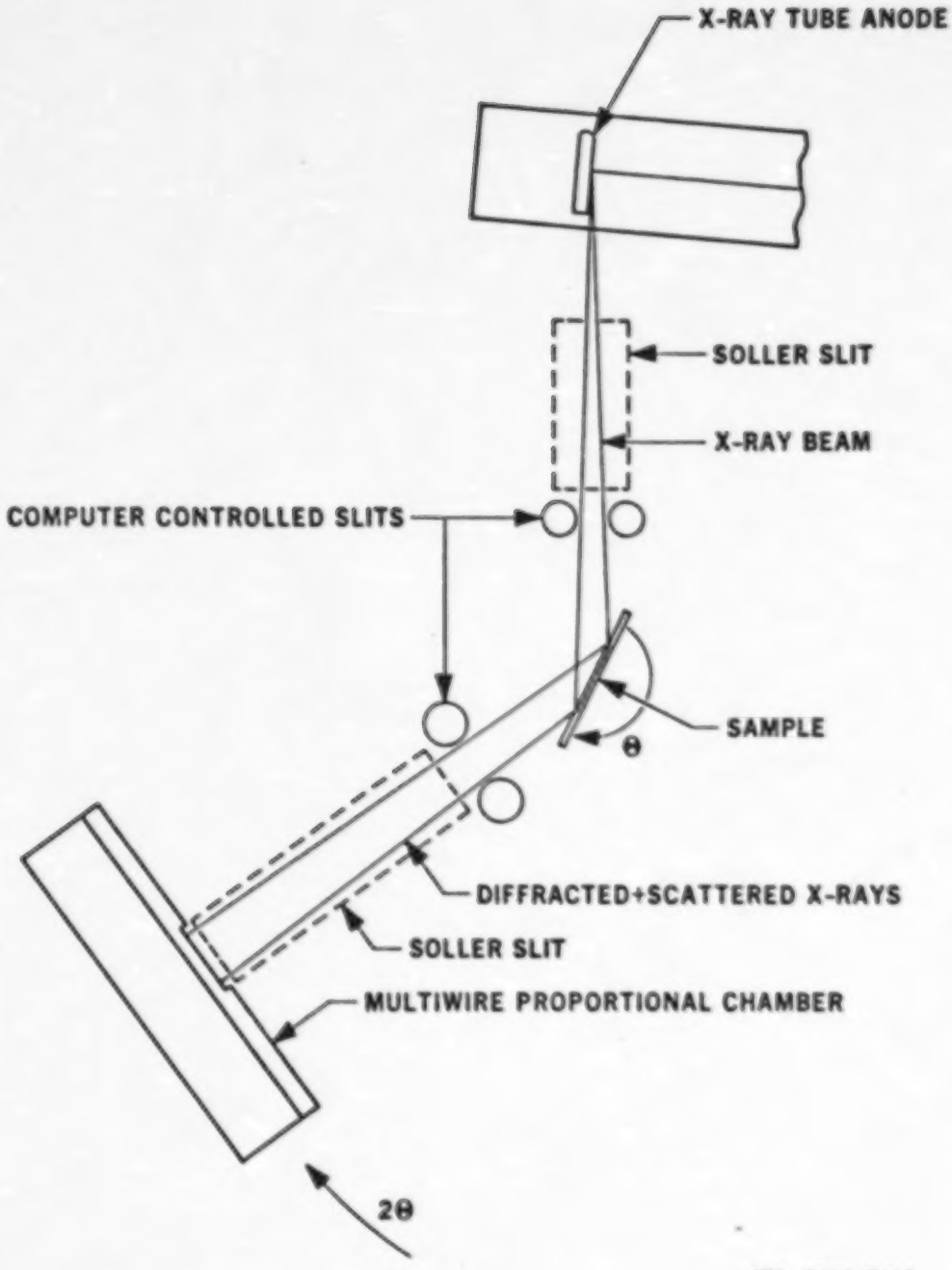


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Fig. 1. General layout of powder diffraction system.

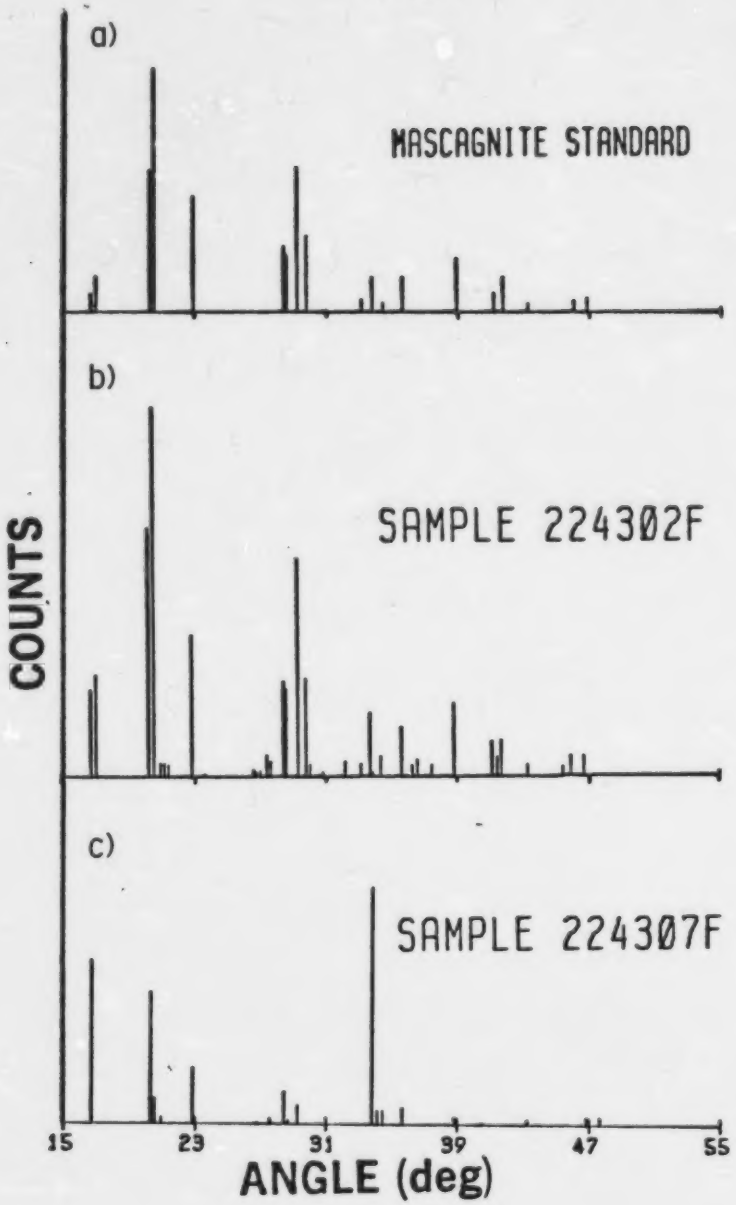


Fig 2. Analyzed peaks from XPD analysis for a)Mascagnite standard b)Sample 224302 fine fraction from Houston aerosol and c)Sample 224307 fine fraction from Houston aerosol.